



**Performance Summary
Of
Quality Control
Reference Samples
SAR-L.1 and SAR-M.1**

R .M. O’Leary and S. A. Wilson

Table of contents

[Introduction](#)

[Development of Reference Samples](#)

[Discussion](#)

[Conclusion](#)

[Table 1. XRAL Analytical Methods](#)

[Table 2. Statistical summary and data plots for SAR-L.1](#)

[Table 3. Statistical summary and data plots for SAR-M.1](#)

Introduction

The two quality control reference samples SAR-L.1 and SAR-M.1 were specifically developed to monitor the quality of analytical results produced by laboratories contracted by the Mineral Resource Program. The data presented here contains a statistical summary of results generated by XRAL, Toronto, Canada, over a 26-month period from 1/1/00 to 2/26/02. Approximately 10% of all samples sent to XRAL were quality control reference samples.

Development of Reference Samples

These reference materials are designed to represent sediment material from a mineralized area, and provide a means to track laboratory performance. Development of SAR-L and SAR-M was guided by four major objectives. The materials should (1) contain detectable element concentrations for the 50+ elements analyzed under the contract, (2) be prepared in sufficient quantity to last 3-5 years at a submittal rate equal to 10% of the total USGS sample load, (3) minimize the occurrence of extraordinary element concentrations which would serve to identify the samples as QC materials to the contract lab, (4) provide a measure of accuracy and precision for contract analysis by having element concentrations in the linear range of each analytical procedure. Because of the requirement that every element required a detectable concentration, it was recognized early in the project, that material would have to be derived from more than one geologic area. The two sites selected to provide the bulk of the material were the Animas River basin above Silverton, Colorado, and the inlet to Chatfield Reservoir near the town of Littleton, Colorado. The sites were selected based on previous studies (Church et al. 19##) and discussions with scientists familiar with the local geochemistry (Crock).

Starting material was sieved in the field (<2mm), and collected in 5 gallon plastic buckets. The samples were transported to the USGS laboratory where they were dried at room temperature in plastic lined trays (2'x 2') for three days, and then transferred back into their original containers. After drying the contents, each bucket was transferred to a 3 ft³ V-blender and mixed for 30 minutes. After mixing, an aliquot of the material was obtained using a sample thief and submitted to the USGS lab for analysis. In the final step the data from each sample (bucket) was entered into a specially designed mixing program which estimated element concentrations in the final material based on element concentrations and mass of each bucket used in the blending stage. Using the mixing program and an iterative approach, two samples, SAR-L and SAR-M, were prepared which represent element concentrations that are two and five times respectively, the determination limits of the contract methods. Bucket sets representing SAR-L and SAR-M

where then ground to <200 mesh (75 micron) using a ball mill and blended in a 10 ft³ V-blender for two days. In the final preparation step aliquots (1-2 oz) of the blended material were transferred by hand to three-ounce cardboard containers. Random selections of six samples were then analyzed at the USGS using ICAP-AES, INAA, WD-XRF, and a series of single element techniques for As, Se, Hg, Total C, Total S, and forms of carbon. A data compilation and statistical analysis produced an average element concentration and standard deviation. The average element concentrations are found in [Table 2](#) and [Table 3](#) as the Target Value.

Discussion

[Tables 2](#), (SAR-L.1) and [Table 3](#), (SAR-M.1) are statistical summaries of the performance of the reference samples from 1/1/00 to 2/20/02, except for C_ICPAES_40 which was limited to 1/01/00 to 3/26/01 due to software restrictions of a maximum 10,000 data points. The tables contain the following information: Method, Element or Species, Units, LLD, Target Value, “n=”, Mean, Sdev, %RSD, %R, Mean -15% and Mean -20%, Mean +15% and Mean +20%, and Pg. The analytical **Methods**, listed in column 1 are described in [Table 1](#). The **Units** are in ppm or %. The **LLD** is the lower limit of determination. The **Target Values** are USGS established values that are used for comparison, and are based on a limited number of determinations and analytical techniques over a short period of time. These values should not be viewed as “Certified Values” such as the NIST Standard Reference Materials. This must be taken into consideration when evaluating the results. The “n=” is the number of determinations. The **Mean** is the average of the values for a give element or species. When 10% or less of the values for a given element or species contain a qualifier of “<”(less than), the qualifier is replaced by a value equal to 2/3 of the LLD. For example, a <1 ppm value is replaced by the value 0.67 ppm. The Mean is accompanied by two measurements of precision; **Sdev** (standard deviation) and **%RSD** (percent relative standard deviation). The **%RSD** is calculated as the standard deviation divided by the mean times 100%. The **%R** (percent recovery) is a measure of accuracy and is calculated as the Mean divided by the **Target Value** times 100%. The next two columns show the brackets of the accepted limits of the analytical performance defined as the **Mean +/- 15%** (values shown in black) or the **Mean +/- 20%** (values shown in red). The last column, **Pg.**, refers to the page number where the plot-graph of the particular element or species can be found.

Plot Viewer, a statistical-graphing module of Labware LIMS, generated the plot-graphs associated with each element. The standard plot shows a line graph of the element or species values, and thin horizontal colored lines representing the average value (green-line), 2 standard deviations (blue-line) and 3 standard deviations (red -line). In addition, two thicker green lines showing the upper and lower control limits and the corresponding statistical summary information were included for the reader’s convenience. In cases where the calculated control limit fell beyond edges the graph, the green lines were placed just outside the upper and lower borders of the graph. A limited number of plot-graphs contain a vertical green line. This condition is created when two or more values are entered into the database and are given the exact same time stamp. To accommodate this situation, the software averages the values and puts one data point on the graph and vertical green line to show the range of values that are represented by the averaged point.

Guidelines for evaluating the data are shown in the following chart that summarizes the ranges of acceptability.

<u>Method</u>	<u>%R (+/-)</u>	<u>%RSD</u>
C_CVAAS_HG	20	20
C_HGAAS_AS	20	20
C_HGAAS_SB	20	20
C_HGAAS_SE	20	20
C_FA_DCP_AU	20	20
C_HGAAS_TL	20	20
C_HGAAS_TE	20	20
C_ISE_F	15	20
C_INAA_W	20	20
C_TOTAL_C	15	15
C_CO2_CARB	15	15
C_Organic_C	15	15
C_TOTAL_H2O	15	15
C_TITR_FEO	15	15
C_TOTAL_S	15	15
C_ICPAES_10	20	20
C_ICPAES_16	15	15
C_ICPAES_40	15	15

When evaluating the data, consideration must be given to the value's proximity to the lower limit of determination (LLD) for an element. As a rule of thumb, the **accuracy and precision tend to degrade as values are within 5X the LLD** and the degradation increases as the value approaches LLD.

Consider the following examples:

<u>Ref. Std</u>	<u>Method</u>	<u>Element</u>	<u>LLD</u>	<u>Mean</u>	<u>%RSD</u>	<u>(Mean)/(LLD)</u>
SAR_L	C_ICPAES_10	Cd	0.05	2.84	6.88	57
	C_ICPAES_40	Cd	2.0	2.58	21.5	1.3
SAR_M	C_ICPAES_40	As	10	36.2	10.4	3.6
SAR_L	C_ICPAES_40	As	10	16.1	17.5	1.6

Gold by C_FA_DCP_AU appears to be a very poor analytical performer with a RSD of 71.6% and 48.1% for SAR-L and SAR-M respectively. However, in this case the poor performance is due to the inhomogeneity of gold in the samples that produces a nugget effect. This was confirmed when determining Au by INAA (Instrumental Neutron Activation Analysis) which also yielded high %RSD values.

Gold by C_ICPAES_10 also suffers from the gold inhomogeneity in addition to many false positive values at the lower end of the detection range. Below is a chart showing the correlation between 914 pairs of samples analyzed by both the C_FA_DCP_AU and C_ICPAES_10 methods.

As can be seen in the chart, ICPAES_10 must have a value of at least 0.8 ppm to have a confidence level of a 100% that a value of at least 0.1 ppm was determined by C_FA_DCP_AU. Also, the discrepancy of values between the two methods as seen by the range of values in the third column can be explained by the sample's size and the method of decomposition. The C_ICPAES_10 used only a 1g sample with an acid-peroxide digestion as compared to the more representative 15g sample of the C_FA_DCP_AU, which uses a fire assay decomposition. Therefore, it is recommended that the C_ICPAES_10 Au be used as a very semi quantitative indicator of gold in the sample.

<u>C_ICPAES_10</u> <u>Values (ppm)</u>	<u>C_FA_DCP_AU</u> <u>% of Sample 0.1 ppm or Greater</u>	<u>Range of C_FA_DCP_Au</u> <u>Values 0.1ppm or Greater</u>
0.1	9 %	0.1 to 1.4
0.2	27 %	0.1 to 1.1
0.3	70 %	0.1 to 6.7
0.4	77 %	0.1 to 0.8
0.5	90 %	0.1 to 6.6
0.6	94 %	0.1 to 0.9
0.7	94 %	0.1 to 1.6
0.8	100 %	0.1 to 2.5
0.9	100 %	0.2 to 0.8
1.0	100 %	0.1 to 2.4

Chromium is the poorest performer of the C_ICPAES_40 package of elements and it's values must be used with caution, more as a semi quantitative value. Chromium has a %RSD of 26.6 and 35.8 for SAR-L and SAR-M respectively due to an inconsistency in the dissolution of the chromium minerals and the inability of the chromium to stay in solution. Chromium values demonstrate a much-improved precision with a %RSD of 10.4 and 11.7 for SAR-L and SAR-M respectively when samples were prepared by a lithium metaborate fusion as determined by C_ICPAES_16.

Tungsten's precision appears marginal with %RSD of 20.8 and 16.9 for SAR-L and SAR-M respectively. However, when the analytical performance was compared with two other INAA labs, the XRAL values seem to fall in the neighborhood of other labs, as can be see in the chart below.

SAR-L W by INAA

	<u>XRAL</u>	<u>LAB A</u>	<u>LAB B</u>
Mean (ppm)	4.33	3.6	3.8
RSD(%)	20.8	18	32

SARM W by INAA

	<u>XRAL</u>	<u>LAB A</u>	<u>LAB B</u>
Mean (ppm)	12.5	11.5	10.8
RSD (%)	16.9	8	15

The Selenium graph for SAR.L shows a number of spikes reaching beyond the upper control limit of 0.14 ppm. Ten of the standards listed below, were selected for reanalysis by XRAL and/or the USGS. The values from the reanalysis validate XRAL's original analyses and indicate that these standard splits contain a higher concentration of Se than the expected 0.9 ppm. The higher concentration encountered may be due to contamination from an unknown source.

Lab #	XRAL				USGS	
	Original Value	Repeat	Repeat	Repeat	Original	Duplicate
C-191722	2.5				2.2	2.4
C-191724	2.1				4.4	
C-191726	2.1				1.9	
C-191864	1.7				2.0	
C-191865	1.8	1.39	2.0	2.4	1.3	2.3
C-191867	1.4	5.85	3.4	1.9	2.0	
C-191869	1.5	2.26	4.1	1.9	3.0	
C-191931	2.7				2.3	2.5
C-191933	2.2				2.1	
C-191935	2.5				2.8	

Conclusion

Overall the data displayed in the tables and plot-graphs have demonstrated a solid level of acceptability. Shown is the ability of certain elements to out perform other elements within the package methods, e.g. C_ICPAES_40, and the degradation of precision at or near the lower detection limit. The study has pointed out problems within the standards such as the particulate nature of gold, and problems inherent with element compatibility with the digestion e.g. Cr in the C_ICPAES_40. Future studies should be directed towards including standards of different sample matrices and concentration ranges.

Table 1. XRAL Analytical Methods

METHOD	DESCRIPTION
C_CO2_CARB	CO ₂ is determined by coulometric titration, carbonate carbon is then determined calculation.
C_CVAAS_HG	Mercury determined by CV-AAS (Cold Vapor-Atomic Absorption Spectrophotometry).
C_FA_DCP_AU	Gold is determined by FA_DCP-AES (Fire Assay-Direct Current Plasma-Atomic Emission Spectroscopy).
C_H2O_TOT	Total H ₂ O is determined by the addition of H ₂ O Plus and H ₂ O Minus, H ₂ O Plus is determine by water removed at 950 ⁰ C, H ₂ O minus is determined by water remove at 105 ⁰ C.
C_HGAAS_AS	Arsenic determination by HGAAS (Hydride Generation-Atomic Absorption Spectrophotometry).
C_HGAAS_SB	Arsenic determination by HGAAS (Hydride Generation-Atomic Absorption Spectrophotometry).
C_HGAAS_SE	Selenium determination by HGAAS (Hydride Generation-Atomic Absorption Spectrophotometry).
C_HGAAS_TE	Tellurium is determined by HGAAS (Hydride Generation-Atomic Absorption Spectrophotometry).
C_HGAAS_TL	Thallium is determined by HGAAS (Hydride Generation-Atomic Absorption Spectrophotometry).
C_ICPAES_10	Ten element are determined by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) using a DIBK extraction.
C_ICPAES_16	Sixteen elements are determined ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) for Majors and selected Trace element using a Li Metaborate fusion.
C_ICPAES_40	Forty elements are determined by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) using a multi-element digestion.
C_ISE_F	Fluoride analysis by ISE (Ion Specific Electrode).
C_NAA_W	Tungsten is determined by INAA (Instrumental Neutron Activation Analysis).
C_ORGANIC_C	Organic carbon is determined by the calculated difference between total carbon and carbonate carbon.
C_TITR_FEO	FeO is determined by a potentiometric titration.
C_TOTAL_C	Total carbon is determined by combustion using a Leco Sulfur Analyzer with an infrared detector.
C_TOTAL_S	Total sulfur is determine by combustion using a Leco Sulfur Analyzer with an infrared detector.

